INVESTIGATION OF THERMAL PROPERTIES OF CARBON FIBRE COMPOSITE WITH PHENOLIC - EPOXY

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SUMMARY : Carbon fibre reinforced composites with phenolic-epoxy (PR-EP) matrix have been recently developed, wherein varying epoxy parts per hundred parts of phenolic resin was incorporated. The combined TGA-FTIR study was conducted for the matrix samples prepared under simulated time-temperature profile used for the preparation of the prepregs. This study enabled determining volatile content and possible structural features of the prepreg. The thermal properties of various matrices and their carbon fibre composites are evaluated in terms of the parameters derived from Thermo Gravimetric Analysis. PR-EP matrices have shown higher thermal stability than neat PR. The technical reasons for improved thermal stability of the matrix are advanced. A little poor thermal performance by carbon fibre reinforced PR-EP composites may be attributed to the formation of inter-phase and non-removal of size material on the carbon fibre surface.

KEYWORDS : Carbon Fibre, Phenolic Resol, Epoxy, TGA & FTIR analysis, Prepreg.

INTRODUCTION

The matrix has been shown to play an important role in the performance of fibrous composite materials (Ref.1). The matrix will not just control the maximum service temperature, due to its glass transition temperature, but also, the moisture sensitivity and the aging properties of the composite. Furthermore, defects induced during processing can often be avoided by adjusting and controlling the resin viscosity and its fibre wetting characteristics. The anisotropic nature of composites further emphasizes the importance of the mechanical properties of the matrix. Both interlaminar and intralaminar properties are affected where low level damage propagation occurs through matrix cracking. Therefore, matrix properties are of primary interest in the development of new composite materials.

Carbon fibre reinforced plastics composites are advanced materials that have high specific strength and stiffness while also possessing excellent high temperature resistance. Epoxy has been the workhorse matrix resin system used with carbon and other advanced fibre based composites (Ref.2, 3). Resin matrix recipe comprising phenol-formaldehyde resin and as well as their structural variants were frequently used in carbon-carbon composite (Ref.2). The matrix composition of epoxy with phenolic resin was reported (Ref.4), wherein the novolac type of phenolic resin was used as a curator of epoxy resin matrix. The advancement in the manufacturing has led to the development of prepreg techniques and the necessity of basic resin system should preferably be in homogenous liquid phase. From these considerations, the combination of phenolic resin with medium viscosity epoxy resin system may become very attractive. The resol phenolic resin has not been used as matrix resin system due to its very short shelf life, the high reactive nature and evolution of volatile matter during its curing reaction. Of late, suitable modifications in the production of resol type phenolic resin have been made, which

have resulted in the development of the resin having long shelf life and moderate viscosity. Although many engineering plastic materials have been possible by the modification of epoxy with phenolic resin, worthwhile studies on carbon fibre reinforced composite with resol type phenolic and epoxy matrix have not appeared in the literature.

As a part of a comprehensive programme on the development of aerospace grade carbon fibre reinforced composite, a unique polymeric matrix comprising of phenolic resol and epoxy resins has been developed at Macromolecular Research Centre, R.D.University, Jabalpur, India and its suitability for carbon fibre composite exhibiting excellent mechanical properties has been demonstrated (Ref. 5,6). Since the application of these advanced carbon fibre composite are intended for use as aerospace structures requiring thermal stability, it is felt necessary to study the thermal properties of these composites with the innovative matrix. In this communication, the results of the investigation on thermal behaviour of the prepreg, matrix and composite have been presented. TGA in conjunction with FTIR analysis have been adopted to study the thermally induced structural changes.

EXPERIMENTAL

Materials

Carbon Fibre: High strength PAN based carbon fibre was supplied by Indian Petrochemicals Corporation Ltd., Vadodara, India. The carbon fibre type INDCARF-25 with 6K-filament count was used. The fibre properties reported by the manufacturer are : Tensile strength 2.5 GPa minimum, Tensile modulus 215 to 240 GPa, ultimate elongation 1.05 to 1.40 %, density 1.78 g/cc and the carbon fibre mass content 93 %. The INDCARF-25 was containing 0.75 to 1.5 % sizing material and carbon fibre tows were used without removing the sizing material.

Diglycidyl ether of Bisphenol-A : This type of epoxy resin (LAPOX B-11) was obtained from M/s Cibatul Ltd., Mumbai, India, which was basically unmodified epoxy resin. The LAPOX B-11 has epoxy value of 5.2 to 5.5 equiv./Kg and its viscosity at 25°C was 0.9 to 1.2 PaS.

Phenolic Resin : The solvent less resol type phenol formaldehyde resin (under the trade name PR-100) was procured from M/s ABR Organics Ltd., Hyderabad, India. The physicochemical characteristics of PR-100 resin are : dark brown liquid, viscosity at (30°C) - 0.6 to 0.9 PaS, pH-7.5 to 7.8 and gel time (at 150°C) – 6 min.

Neat Matrix and Composite Preparation : Five matrix resin compositions were prepared by taking hundred parts of PR-100 resin with 0, 50, 100, 150 or 175 parts of LAPOX B-11 respectively & designated as PR-EP-0, PR-EP-1, PR-EP-2, PR-EP-3 and PR-EP-4 respectively. The matrix resin compositions having 200 or more parts of epoxy resin were not used as they showed tackiness after full curing. For the prepreg preparation, the matrix resin were coated uniformly over the carbon fibre and were heated at 140°C for 2-4 min and were immediately cooled to room temperature to get a carbon fibre prepreg. The prepreg was prepared in equipment designed and fabricated in-house. The composites were prepared in leaky type three parts split mould made up of mild steel. The composites were prepared by laying up in one direction (0 degree) and utmost care was exercised in the preparation of the unidirectional composites. The fibre volume fraction was kept close to 0.6 in all composites. The curing conditions employed were two step heating viz., 150°C for 2h and followed by 200°C for 4h. No

pressure was recorded for the mould as only manual tightening was followed. The fibre composites are designated as PR-EP-COM-0, PR-EP-COM-1, PR-EP-COM-2, PR-EP-COM-3 and PR-EP-COM-4 respectively for those having PR-EP-0, PR-EP-1, PR-EP-2, PR-EP-3 and PR-EP-4 matrix resins.

Cure Extent Study by FT-IR Analysis : The FT-IR spectra of the neat phenolic resin (PR) and epoxy resin (EP) were taken. Perkin Elmer's FTIR spectrophotometer model 1720 X was used and data compilation and analysis were done with the help of PE 3700 data station. The FTIR spectra for the sample of neat PR and PR-EP compositions were taken at different stages, i.e. at prepreg stage (140°C for 4 and 6 min) and fully cured stage (150°C for 2h and followed by 200°C for 4h). The prepreg preparation was done by heating the samples in TGA furnace and FTIR spectra were taken using KBr pellet of the samples.

Thermogravimetric Analysis (TGA) : Thermogravimetric Analyzer of Perkin-Elmer (Model No. TGA-7) equipped with a 7700 computer was used to study the thermal degradation pattern and the thermal stability of the sample of matrices and composites. The weight loss during prepreg preparation were studied by simulating the time-temperature heating conditions in TGA. First, samples were heated upto 120°,130°, 140° and 160°C and the heating was continued for 2,4 and 6 min. respectively at each temperature. The heating rate of 100°C/min was adopted during dynamic heating to achieve the target temperature used for isothermal TGA.

Thermograms (under dynamic heating) were obtained at constant heating rate of 20°C/min and was recorded from 50°C to 900°C. Experiments were carried out under analytical grade nitrogen atmosphere (IOLOAR of M/s IOL, New Delhi, India), at the purge rate of 2 to 3.5 psi.

Following TGA derived parameters were determined from the various thermogrames :

1. Initial decomposition temperature (IDT) i.e., the temperature at which actual decomposition of the sample starts.

2. Ultimate decomposition temperature (UDT) i.e., the temperature at which the rate of weight loss was maximum.

3. Temperature at 50% decomposition ($D_{1/2}$).

4. Percentage residue i.e., the amount of residue left at maximum temperature (900 ^{0}C).

5. Energy of activation (E_a) of decomposition.

The activation energy of decomposition of matrices and composites were evaluated by using integral equation of Coats and Redfern (Ref.7).

$$\mathrm{Log}_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] = \log_{10}\frac{\Delta R}{\Delta E}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3\,RT}$$

For all values of 'n' except n=1 in that case

$$\mathrm{Log}_{10}\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log_{10}\frac{\Delta R}{\Delta E}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3\,RT}$$

Where,

T	=	absolute temperature (°K)
E_a	=	Activation Energy (cal/mole)
R	=	Gas constant (1.987 cal/mole/°K)
α	=	Wi-Wt/Wi-Wf = Fraction Decomposed
Wi	=	Initial weight
Wt	=	Weight at given temperature
Wf	=	Final weight

The best fit value of 'n' was calculated in the range of 0-2 and $-\log_{10}[\log_{10}(1-\alpha)/T^2]$ was plotted against 1000/T (°K). By computational approach, value of 'n' was selected which gave the best straight line through the point. Activation energy (E_a) was calculated from the slope of plot using following equation :

$$E_a = 2.303 \times R \times \text{slope}.$$

RESULTS AND DISCUSSION

The innovative feature of resol phenolic-epoxy matrix lies in the fact that almost stoichiometric conversion of these two resins to an adduct takes place at the fact almost stoichiometric conversion of these two resins to an adduct takes place at the prepreg stage itself. The formation of the adduct has been qualitatively studied in our previous study (Ref.5) where in the epoxy group as a consequence of the addition of phenolic hydroxyl and epoxy functional groups was monitored. In order to facilitate the study of quantitative conversion of the resins to the intermediate adduct , a combined TGA and FTIR analysis has been chosen here. A very small (3 to 5 mg) sample of phenolic-epoxy mix was heated in the pan of TGA furnace under simulated time-temperature conditions prevailing during prepreg preparation. The samples were heated under dynamic condition at adequately higher heating rate to achieve the temperature at which the prepreg reaction takes place. The samples were withdrawn after known time isothermal heating and were characterized by FTIR spectroscopic analysis. The consumption of the epoxy was monitored (Ref. 8) from the peak ratio at 914 cm^{-1} (characteristics of epoxide ring stretch) and 1500 cm^{-1} (assigned to semicircle stretching of benzene ring). The loss of volatile during the dynamic heating to targeted temperature and isothermal heating at targeted temperature for given duration have been determined from the weight loss data in TGA analysis. For the briefness of the discussion the results of the resin matrix PR-EP-1 and the prepreg preparation temperature of 140°C have been presented, although, the data for all the matrix compositions and the other temperature (120°, 130° & 150°C) have been generated. The typical data for the prepreg preparation of PR-EP-1 sample at 140°C has been shown in Table-1.

Table 1 : Simultaneous TGA-FTIR studies for prepreg preparation with PR-EP-1 resin matrix

S.No.	Tempe--rature (°C)	Heating time (min)		TGA studies			Epoxy consumption (%) as per FTIR studies
				Weight loss (%) during			
		Dynamic Heating	Isothermal Heating	Dynamic Heating	Isothermal Heating	Total	
1.	Room Temp.	0	0	0	0	0	0
2.	140°C	1.4	2	9.21	3.17	12.38	18
			4	9.21	4.21	13.42	78
			6	9.21	4.20	13.41	88
3.	*Full Curing	150°C 2h & 200°C 4h		2.0	-	2.0	100

* The full curing has been done in lab oven and not in TGA furnace.

The result of this experiment performed at 2,4 & 6 min have indicated that the total volatility at the prepreg stage varies form 12.4 to 13.4 %, where as, the epoxy consumption goes up from 18 to 88%. These result have shown that most of the epoxy groups are consumed at 4 min. of prepreg preparation at 140°C. The fact that only adduct formation takes place and not the primary phenolic resin curing was established only qualitatively by comparing the absorption peak ratio at 2900 cm^{-1} (the methylene CH stretching) and 1500 cm^{-1}. Since there is no change in the absorption peak ratio (2900/1500) by dynamic and isothermal heating during prepreg preparation, it indicated that the curing reaction (characteristics of phenolic resin) did not take place. The Fig.1 shows the typical FTIR spectra for PR-EP-1 matrix composition at different stages i.e. from the time of mixing up two resins at room temperature prepreg preparation stage at 4 & 6 min. and full curing of the matrix. The disappearance of the characteristic absorption band at 914 cm^{-1} for epoxy after 6 min. of prepreg preparation provide the basis for the PR-EP adduct formation. The likely chemical reaction for the PR-EP adduct formation and subsequent curing of the said adduct is described in reaction scheme (Fig.2). The thermal stability of the composite could be assessed in terms of the TGA derived parameters especially IDT, $D_{1/2}$ and activation energy of thermal decomposition (E_a). The TGA derived parameters were determined for all matrix compositions and the neat uncured epoxy resin. Various TGA derived parameters for all matrix compositions have been calculated from the thermograms and are presented in Table 2.

Table 2 : TGA derived parameters for PR (Neat), EP (Neat) & PR-EP matrices at varying epoxy php

Sample Designation	Epoxy php	IDT (°C)	UDT (°C)	$D_{1/2}$ (°C)	Residue content (%)	E_a (Kcal/mole)
PR (Neat)	00	248	606	433	68	8
PR-EP-1	50	408	466	433	29	44
PR-EP-2	100	408	469	439	30	47
PR-EP-3	150	412	473	439	30	48
PR-EP-4	175	416	471	441	31	47
EP (Neat)	-	380	409	389	0.0	37

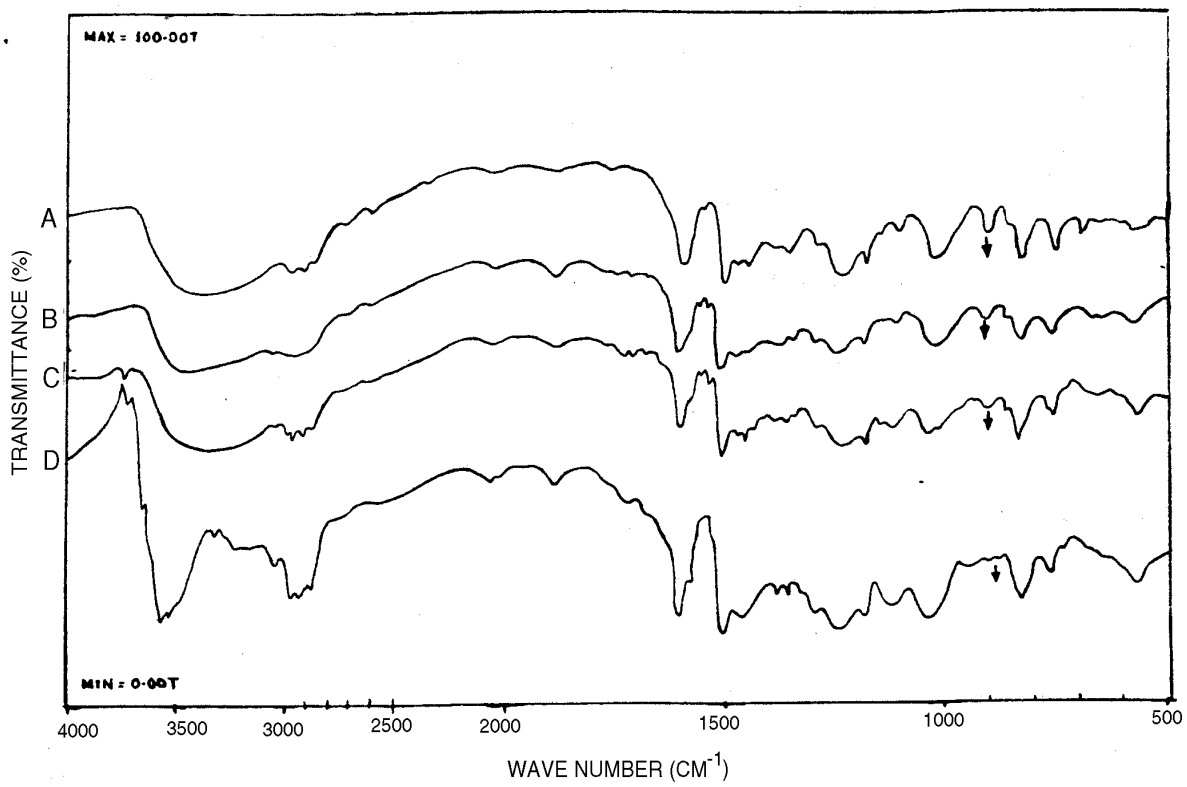

Fig.1 : FTIR spectra of PR-EP-1 Matrix at different stages of curing (a) At room temp. (b) at prepreg stage at 4 min (140°C) (c) prepreg stage at 6 min (140°C) and (d) after full cure (150°C at 2h & followed by 200°C for 4h).

The values for the neat epoxy resin (the one used for PR-EP) is also given in Table 2. It can be seen that the IDT value for PR-EP compositions have shown the values over 210°C higher than that of the neat PR. Nevertheless, the UDT value for the PR neat is higher by over 150°C than the PR-EP compositions. The values for $D_{1/2}$ for PR-neat as well as most of the PR-EP composites remains more or less same. It can be inferred from these data that the PR-EP compositions are relatively more stable than its neat PR and neat EP. This is further supported by the values of the energy of activation for decomposition calculated for all cured samples. The PR neat has shown only 8 Kcal/mole for E_a whereas the PR-EP compositions have shown E_a values ranging from 44 to 48 Kcal/mole. The uncured neat EP has E_a value of 37 cal/mole. The relatively enhanced energy of activation may be attributed to the formation of adduct intermediate at prepreg stage followed by its curing. It can be posulated that the cured PR-EP will be different structurally than the cured PR resin. These aspects are being studied in depth and will be communicated soon. The another interesting result is residue content of the various matrix composition. The neat PR has given the residue to the extent of 68% which has been found in many studies including the recent one by Bindu *et.al.* (Ref.9). All the PR-EP matrix compositions have given 29 to 31% residual char. The constant value of the residue content in PR-EP composition having varying epoxy php could be rationally explained by the chemical structure of the cured resin, as given in Fig.2. It can be presumed that the residue content is

mostly governed by the chemical structure of the cured resin which does not contain phenolic moieties as the phenolic groups get completely consumed by the reaction of epoxy resin.

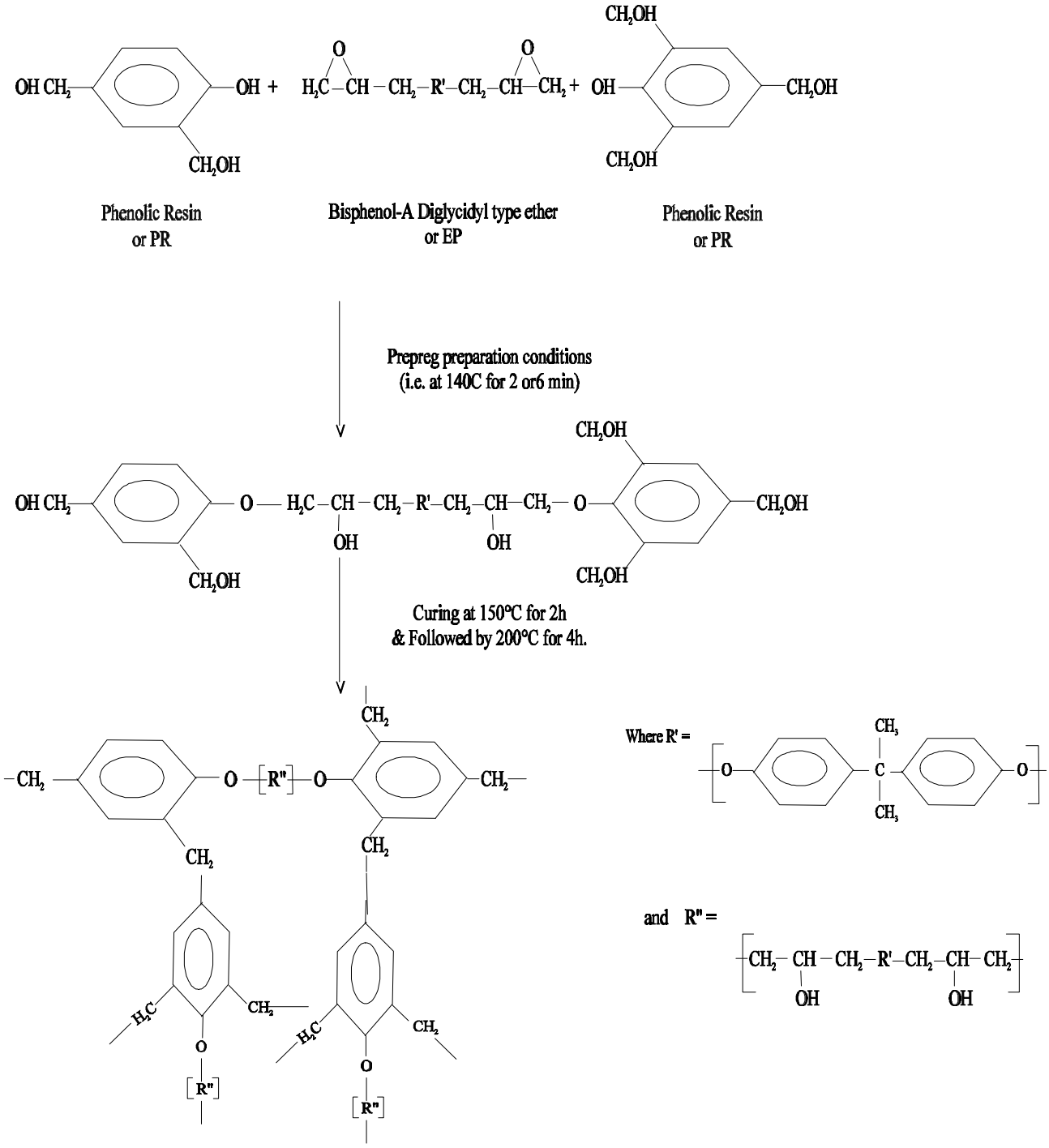

Fig. 2 : The reaction scheme describing PR-EP adduct formation and its curing.

The thermal stability of the composites of the carbon fibre using neat PR and different PR-EP matrix has also been studied by thermogravimatric analysis technique. Various values for TGA derived parameters for carbon fibre composite with different PR-EP matrices are given in Table-3. The carbon fibre composites have exhibited the similar thermal stability trend as shown

by their respective matrix. The IDT value for PR-EP-COM-1, PR-EP-COM-2, and PR-EP-COM-3 are 40-50°C lower than the respective matrix and this could be due to the poor thermal

Table 3 : TGA Derived Parameters For Carbon Fibre Composites With Different PR-EP Matrices

Sample Designation	Epoxy Php	IDT (°C)	UDT (°C)	D1/2 (°C)	Residue content (%)	E_a (Kcal/mole)
PR-EP-COM-0	0.0	248	606	433	84.2	7.00
PR-EP-COM-1	50	342	452	496	75.6	35.00
PR-EP-COM-2	100	362	458	410	73.0	37.00
PR-EP-COM-3	150	373	446	413	72.0	36.60
PR-EP-COM-4	175	408	508	458	71.5	32.50

decomposition of carbon fibre in the IDT region. The UDT and $D_{1/2}$ values are found to be more or less same as exhibited by their matrices. The char content as shown as residue for the carbon fibre composite is the sum of the char contents given by carbon fibre and the residue given by the respective matrix resin. The values of E_a as calculated from TGA for carbon fibre composite are lower than the corresponding values for the matrix resin. The E_a value for composite having neat PR has been 1 Kcal/mole lower than the neat PR matrix whereas the E_a values of the carbon fibre composites are down by 10-12 Kcal/mole than their corresponding E_a values of resin matrix alone. There could be two possible reasons for the lower E_a values of the composite than that of their matrices. The size material over the carbon fibre may be the first cause of lowering the E_a values of the composites as sizing was not removed during the prepreg preparation. The second reason could be due to poor thermally stable interphase formed between carbon fibre and matrix. The experimental support for such a little abnormal observations could not be generated for lack of suitable analytical technique. The investigations on the thermal behaviour of PR-EP matrices and their carbon fibre composites have established that PR-EP composites are far more thermally stable than their neat PR counterpart.

CONCLUSIONS

A carbon fibre reinforced composites with phenolic epoxy matrix containing varying ratio of PR & EP have been prepared for the first time. The combined TGA-FTIR study was conducted to determine the loss of volatile during prepreg preparation and to characterize them. The thermal stability of the matrix resins and their carbon fibre composites has been evaluated by Thermo Gravimetric Analysis and its derived parameters. The relatively higher thermal stability has been exhibited by PR-EP resin matrix than neat PR, however, the composites have shown a little lower thermal stability than matrix counterparts.

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REFERENCES

1. Seferis, J.C. and Nicolais, L., *The Role of the Polymeric Matrix in Processing and Structural Properties of Composites Materials*, Plenum Press, New York, 1983.
2. Donnet, Jean-Baptiste and Bansal, Roop Chand, *Carbon Fibres*, Marcel Dekker Inc, New York and Basel, 1984.
3. Manocha, L.M., Bhatt, H. and Manocha, S.M., "Development of Carbon/Carbon composites by Co-carbonisation of phenolic resin and oxidised Pan Fibre", *Carbon*, Vol. 34, No.7, 1996, pp. 841-849.
4. Paul, S., "Crosslinking : Chemistry of Surface coatings", *Comprehensive Polymer Science (Sixth Volume)*, Ed., Press, Oxford, England, 1989, Ch.6, pp. 144-192.
5. Varghese, S., Yadav, P., Jain, S., Ghuratia, S. and Nema, S.K., "Mechanical Characterization of Carbon Fibre Reinforced Phenolic Resol and Epoxy Condensate Planstic", Paper Orally presented in International conference on Polymer Characterization 'Polychar-5' held at University of North Texas, Denton, USA, Jan. 7-10 1997 & Accepted for Publication in Polymer Engineering & Science.
6. Varghese, S., Yadav, P., Ghuratia, S., Verma, M.M., Hansraj & Nema, S.K., "Innovations in Carbon fibre Modified Phenolic Composites for Aerospace Application", Proceedings of Nineteenth International SAMPEE Europe Conference, Paris, France, April 22-24 1997.
7. Coats, A.W. and Redfern, J.P., "Kinetic Parameters from Thermogravimetric Data", *Nature*, Vol. 201, 1964, pp. 68-69.
8. Zaks, Y., Jeelan, L.O., Raucher, D. and Pearce, E.M., *Journal of Applied Polymer Science*, Vol. 27, 1982, pp. 913-930.
9. Bindu, R.L., Reghunadhan Nair, C.P. and Ninan, K.N., "Addition-cure Phenolic Resin Based on Propargylated Novolac", Proceedings of the International symposium on Polymer Beyond AD 2000, New Delhi, India, January 12-15, 1999, Ed., Anup K. Ghosh, pp. 138-141.